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Dating of Ancient Ceramics by Thermoluminescence

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The present investigation was undertaken as a preliminary experiment on thermoluminescence dating of ancient pottery. The natural glow-curve resulting from ancient pottery was found to differ from the artificial glow-curve after Co^{60} gamma-ray irradiation in shape in the low temperature region. In the case of the Yayoi pottery, these two glow-curves were found to be similar in shape in the high temperature region for the sample prepared by washing and separating the grain. Thus, this technique is suggested to be favourable for the measurement of the absorbed dose of ancient ceramics. However, with the natural glow-curves of the Jomon and Sue potteries, the deformation of the glow-curve was observed even in the high temperature region. The results of chemical analysis showed that these samples contained some amount of changeable or organic material. The more research seems to be necessary to find any better method for the preparation of these samples.

INTRODUCTION

Ancient pottery has played an important role as a standard for the determination of the archaeological age. In archaeology, the age of ancient pottery has been determined by stratigraphy where it was dug out, as well as by its type. However, the age determined by this purely archaeological method is only a relative one. The present-day ways to determine the absolute age of ancient survivals are only well-known radio-carbon dating and the method of observing thermoluminescence here reported.

The radio-carbon dating has recently made a remarkable progress, however this method is not always adequate for pottery, because its object should be an organic material which ancient pottery does not contain. By this method the shell and charcoal of the Jomon era in Japan were estimated to be older than the general archaeological age, but this result still remains open to question. Since all the scientific methods of dating contain some assumptions, it is indeed necessary to examine the results obtained through methods basing on different principles. Therefore, we have tried to develop quite a new method of dating by thermoluminescence in which the age can be determined by the radiation energy stored in the pottery.

Although thermoluminescence has been known since the 17th century, the accurate measurement of thermoluminescence has recently become possible with the development of multiplier phototubes. In recent years, several groups of workers have made basic researches on the properties and the formation mechanism of electron and hole trapping centers on alkali halide irradiated by radiation.

There are also published some reports on application of this phenomenon such as on thermoluminescence dosimeters employing synthetic crystals of manganese-

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activated calcium fluoride¹⁾ and manganese-activated calcium sulfate²⁾. Those dosimeters have high sensitivity (for doses as low as 20 μ r) and excellent linearity to absorbed dose. We succeeded also in estimation of the atomic bomb radiation of twenty years ago, making use of roof-tiles as phosphor irradiated the radiation from the bombs in Hiroshima and Nagasaki³⁾. Measurements of the radiation-induced thermoluminescence of some substances in nature irradiated for long period can be used to find the radiation dose absorbed by these substances in the past. Several years ago, measurements of thermoluminescence of carbonate sediments was found to be applicable for the geologic age determination. Thermoluminescent dating of ancient ceramics was first attempted by Kennedy⁵⁾ with sixteen sherds of the Greek pottery, and he proposed its advantage over radio-carbon dating. The presence of chemiluminescence from ancient ceramics heated in air has recently been pointed out by Aitken *et al.*⁶⁾ In examining this phenomenon carefully they found that the specific glow of some ancient ceramics is in proportion to the age.

In order to remove the oxygen effect as well as to increase the sensitivity of glow intensity from the sample, we separated the sample by means of a magnetic separator. The glow-curves obtained through this treatment are presented in this paper.

PRINCIPLE

The ancient ceramic material contains some radioactive elements, such as uranium, thorium and potassium, so that the ceramics receive the radiation coming from those elements. Some of this energy is stored at lattice imperfection as trapped electrons. When ceramics are heated up to 500°C, the trapped electrons are ejected from their traps by thermal agitation, and then recombine with a luminescence center to emit light. Thermoluminescence is generally studied by the glow-curves which record the luminescence intensity as a function of the temperature.

The thermoluminescence intensity of natural glow for ceramics is proportional to the number of the trapped electrons, which is also proportional to the absorbed dose. Since the magnitude of an accumulation of energy is proportional to the dose received since the last heating, if the trapped electrons have enough long life, the intensity I can be expressed as $I=kD$, where D is the absorbed dose integrated over the age, and k , a proportional constant, is called the susceptibility for radio-thermoluminescence. The intensity of artificial glow by irradiation with a standard source, I_0 , is written as $I_0=kD_0$. Thus, we obtain $I/I_0=D/D_0$. Also, the absorbed dose of ancient ceramics may be expressed as $D=cRt$, where R is counting rate of α -ray, t is the age of a pottery and c is a constant which can be calculated. Thus, t is given as $t=D_0/cR \times I/I_0$.

EXPERIMENTAL PROCEDURES

A piece of the ancient pottery was ground with an agate mortar after a thin layer of the surface of the piece was removed. The powder was sieved by means of a standard sieve so that its standard grain 100~200 mesh might be obtained. It was washed in water and then in alcohol to remove absorbed dusts on the

mineral surface. By this procedure it would be expected to facilitate separation of the sample and to increase the sensitivity of glow intensity and to remove the effect coming from organic or other impurity in surface.

The powder was separated into colourless and coloured minerals by means of a magnetic separator, and the former ones was used to the thermoluminescence measurement, because these seemed to give high sensitivity and free from complex minerals. The amount of the sample powder thus obtained was a third of the total or less.

The experimental apparatus used to measure the thermoluminescence was described in the previous report,³⁾ excepting that the band-path filter was used to reduce the black body radiation. In the present case as a filter a Toshiba VV-40 was used. This improvement gave better results.

The glow-curves resulting from the natural radiation and the calibration curves were obtained by the following procedures. 300 mg of the powder, separated by the above treatment was spread uniformly over the hot plate (25 mm ϕ) and was pressed onto the plate. The sample was heated at a rate of 130°C/min until the themperature reached 450°C, and glow-curve, contributed from the natural radiation, was recorded. Then the sample was cooled and heated again in the same manner as before to record the background glow-curve, i.e., black body radiation.

Since the thermoluminescence sensitivity of different ceramics is not the same calibration should be made for each sample. The same sample was first exposed to Co⁶⁰ gamma rays (1000 Curies source). After it had absorbed a known amount of gamma dose, the new glow-curve was recorded as before. This glow-curve was superimposed on the natural glow-curve in order to compare these two curves easily.

RESULTS

As preliminary tests, the ancient pottery of the Jomon, Yayoi and Sue era in Japan, shown in Table 1, was surveyed to observe the glow-curve resulting from the separated colorless fractions of the sample.

Table 1. Samples

Sites	Materials	Dates
Ishiyama, Shiga	Potsherds of Earliest Jomon Period	VI Millennium B. C.
Nakagaito, Osaka	Potsherds of Early Yayoi Period	1st cen. B. C.
Kiln No. 21, Tokiyama, Osaka	Sue Ceramics of Nara Period	1st half of 8th cen. A. D.

As the result, the natural glow-curves obtained from the Yayoi pottery showed the shape which we had expected. This type of the glow-curves obtained is shown in Fig. 1, where the glow-curve resulting from the Co⁶⁰ gamma-ray irradiation is superimposed on the natural glow-curve for comparison. Since the mineral composition of ceramic material is complex, it has many groups of trapping level. Therefore, its glow-curve does not show any distinct glow peak which is contri-

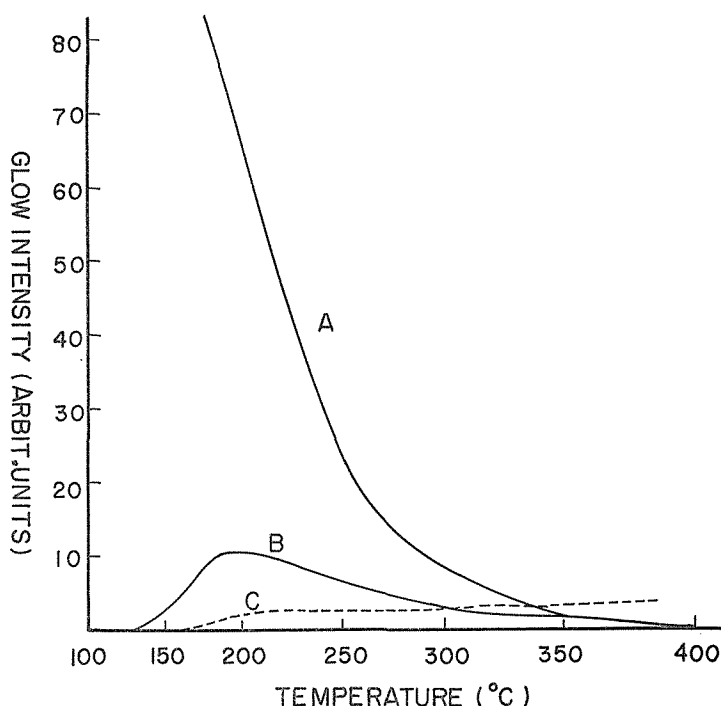


Fig. 1. Glow-curves for the Yayoi pottery.

- (A) Thermoluminescence after irradiation with gamma rays from Co^{60} (approx. 1×10^3 r), (colourless fraction).
- (B) Thermoluminescence from natural radiation (colourless fraction).
- (C) Thermoluminescence from natural radiation (coloured fraction).

buted by a few discrete trapping levels, but shows a very broad peak.

A comparison of the two glow-curves, natural and artificial, shows that the former decays at the part of the low temperature region. Such change of the glow-curves arises from the decay at the normal temperature since the last heating. As for the part of the high temperature region, both of these glow-curves show nearly the same shape. Therefore, the type of the glow-curve as shown in Fig. 1, is desirable for the measurement of the absorbed dose. We used such samples showing the above type of glow-curve to estimate the atomic bomb radiation²⁹.

The glow-curve for the coloured fraction of separated sample is also shown in Fig. 1. In this case, it is seen that its intensity is about a quarter of the glow resulting from the colourless fraction and has not any broad peak. This fact shows that the coloured fraction is an unfavourable sample.

The natural glow-curve resulting from the colourless fraction of the Jomon pottery is shown in Fig. 2, with the glow-curve from the same sample irradiated by gamma rays from Co^{60} . This natural glow-curve shows that the thermoluminescence intensity decreases gradually as compared with that from the irradiated sample, so that two glow-curves do not show the same shape even at the part of the higher temperature. It seems that this deformation is contributed by organic impurity which contaminate the surface of the grain. The chemical analysis of

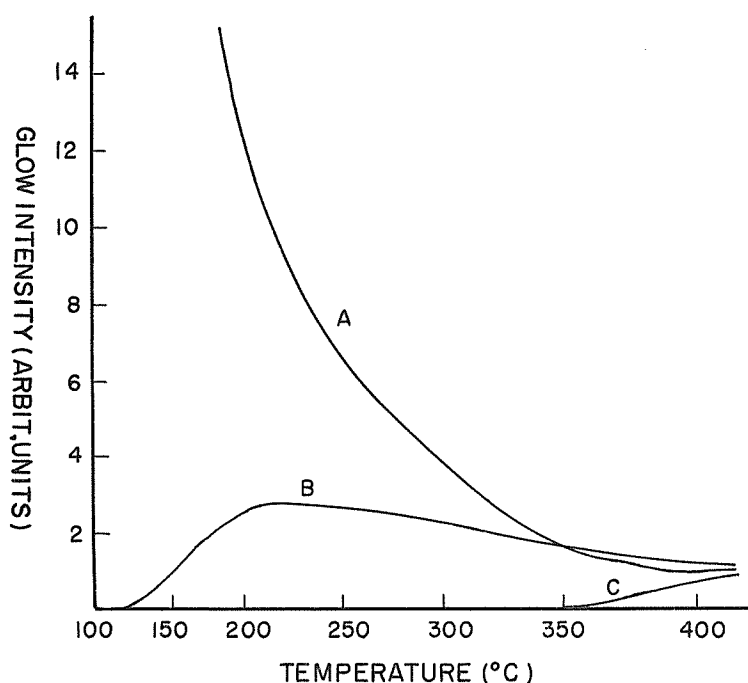


Fig. 2. Glow-curves for the Jomon the pottery.

- (A) Thermoluminescence after irradiation with gamma rays from Co^{60} (approx. $1 \times 10^3 \text{ r}$), (colourless fraction).
 (B) Thermoluminescence from natural radiation (colourless fraction).
 (C) Black body radiation.

Table 2. Results of chemical analysis.

Sample	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	Na_2O	K_2O	TiO_2	MnO	P_2O_5	H_2O	Org anic*	Total	Ign. loss
Jomon	59.86%	19.29	Tr	2.74	0.53	1.83	2.02	1.35	0.36	0.11	0.06	5.27	5.86	99.28	12.11
Yayoi	53.30%	24.62	5.73	1.43	0.78	1.56	1.43	2.11	0.39	0.08	2.90	6.54	Tr	98.97	8.09
Sue	67.12%	23.34	1.00	3.57	0.52	0.55	1.28	2.28	0.44	0.04	0.05	0.22	Tr	100.41	0.16

* Material of insoluble in $\text{H}_2\text{SO}_4 + \text{HF}$.

the pottery used in the present work showed some amount of carbon contained in the sample. The results are given in Table 2.

As for the natural glow-curve of the Sue pottery we could not observe any broad peak owing to chemiluminescence. This fact may be due to that the Sue pottery was heated in reducing condition when it was manufactured and its separated sample was much contaminated by impurity even after the washing.

CONCLUSION

As we have observed, the thermoluminescence intensity of the ancient pottery gives some information about the absorbed dose integrated since the last heating. If any adequate improvement would be made in sample preparation, the thermoluminescent dating will be an effective one for the age determination of the ancient pottery.

The fact that the natural glow-curve shows the deformation at the part of the high temperature has a baneful influence upon an accurate measurement of the absorbed dose. The following two methods are considered to be free from such a deformation. One is the nitrogen technique, where the measurement is performed under nitrogen to be free from the oxygen effect, as adopted by Aitken and his collaborators.⁶⁾ The other is the sample preparation technique of washing and separation of the powder, employed in our experiment, although it should be improved. There remains yet problems to be solved such as to find the most effective artificial radiation source to be used for comparing susceptibilities of various samples.

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